

[54] **METHOD OF MAKING A JOINED METAL STRUCTURE**
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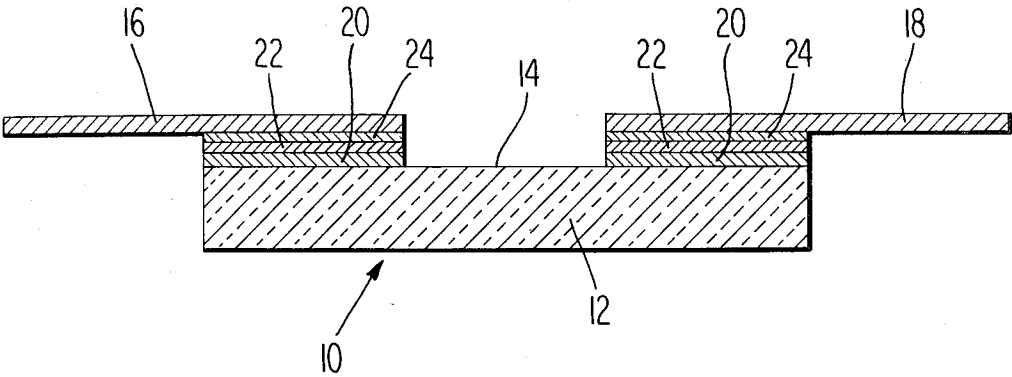
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ABSTRACT

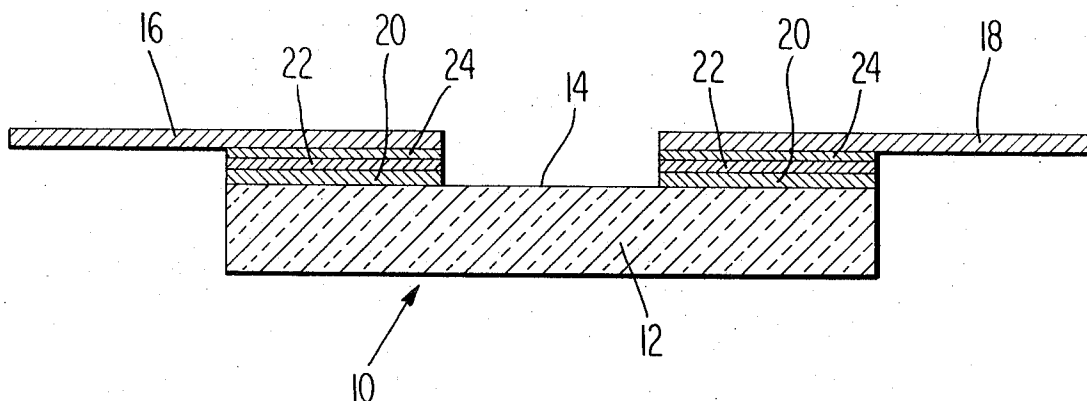
A ceramic-to-metal joint in which a metal is brazed to a molybdenum metallized ceramic after first coating the molybdenum with palladium. The palladium is preferably plated onto the molybdenum by a chemical displacement process.

4 Claims, 1 Drawing Figure



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METHOD OF MAKING A JOINED METAL STRUCTURE

This is a division of application Ser. No. 91,363, filed Nov. 20, 1970, and now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to joined metal structures such as ceramic-to-metal joints or seals, and to their method of manufacture.

In a known form of ceramic-to-metal joint there is a coating of molybdenum or molybdenum-manganese alloy fused to a ceramic body, a copper or nickel layer plated on the alloy, and a metal body brazed to the plated, metallized ceramic. The plated copper or nickel layer is provided to improve the wetting characteristics of the molybdenum surface and to prevent oxidation thereof. Without such a layer, it is not possible to make a secure brazed joint to molybdenum. The brazing materials are generally alloys of copper, silver, nickel, or gold. Metals to which ceramics can be brazed in this way include copper, nickel, tungsten, molybdenum, iron, nickel alloys, and iron alloys.

Nickel is used more frequently than copper as the plated layer on molybdenum coatings. The application of the coating is done in a relatively large electrolytic or electroless plating bath which is used continuously. The composition of the bath is maintained by adding nickel from time-to-time to replace the material which is plated out onto the work pieces. Inherent in this process are contamination and loss due to waste and plating out of nickel onto the surfaces of the container and the work piece handling equipment. Because of these losses, the use of nickel is relatively costly. Moreover, a smooth adherent coating is difficult to obtain. The coating often exhibits bubbles and is permeable to contaminants.

The molybdenum coating in prior ceramic-to-metal joints has been plated with metals other than nickel and copper. Some of the metals of the platinum family, namely, platinum, iridium and rhodium have been used, but palladium has not. The named platinum family metals have been used as a barrier to prevent undesirable interaction (perhaps related to the bubbling noted above) between a nickel layer or a nickel containing brazing alloy and the molybdenum coating. Palladium has been avoided presumably because it is highly soluble in molybdenum and most common brazing alloys at brazing temperatures and cannot, therefore, be regarded as a barrier between these materials and the molybdenum coating.

THE DRAWING

The single FIGURE of the drawings is a cross sectional view of a ceramic integrated circuit package in which the electrical leads are bonded to a ceramic substrate with the present joint structure and by the present method.

DETAILED DESCRIPTION

The structure of the present novel joined metal structure is illustrated in the drawing as utilized in an integrated circuit package 10. The package 10 includes a substrate 12 which may be of a beryllia or alumina ceramic material and which has surface 14 adapted to support an integrated circuit semiconductor chip (not shown). Electrical leads 16 and 18 are brazed to the ce-

ramic substrate 12 by the present novel process to be described hereinafter. The leads 16 and 18 may contain nickel, iron, nickel containing alloys, or iron containing alloys. Preferably, these leads are "Kovar."

The leads 16 and 18 are joined to the substrate 12 by brazing. The substrate 12 carries on the surface 14 thereof a joined coating 20 of molybdenum or molybdenum-manganese alloy. This coating is used in prior ceramic-to-metal joints and seals and its application is conventional.

As shown in the drawing, there is a layer 22 which is deposited on and bonded to the molybdenum coating 20. The layer 22 is palladium in the present novel structure. It is not known whether this layer 22 exists as a discrete layer after the completion of the brazing operation or whether it is partially or completely dissolved in the molybdenum or in the brazing alloy. It is shown here as a separate and distinct layer for convenience. The remaining layer shown in the drawing is a body of brazing alloy 24 which may be initially a preform of the brazing material. The brazing material is copper, silver, a copper containing alloy and/or a silver containing alloy. Preferably, the brazing material 24 is a copper-silver alloy. Palladium is highly soluble in this material at brazing temperatures so that whether or not any part of the palladium layer 22 remains as a discrete layer after the brazing operation at least some of it will dissolve in the brazing material, and there will be a high concentration of palladium in solid solution in at least the region of the brazing material which is adjacent to the molybdenum coating 20.

The present novel method includes the application of the palladium coating 22 to the conventionally applied molybdenum coating 20. Preferably, the palladium coating 22 is applied by an electroless chemical displacement process in which the substrate 12 with the molybdenum coating 20 thereon is immersed in a palladium displacement plating solution of a type which is available commercially. For example, the solution may be one called "DNS Palladium Immersion Solution" produced by the J. Bishop & Company, Platinum Works, Malvern, Pennsylvania. This material is based on a solution of the complex of potassium dinitrito-sulphato-palladate, $K_2Pd(NO_2)SO_4$. It is supplied as a concentrate containing 50 grams per liter which may be diluted with deionized water to any desired concentration. The parts to be plated are immersed in this solution for a time sufficient to deposit the required thickness of palladium. The manufacturer recommends a dilution of about 4:1 and a plating time of about 30 minutes at between 20° and 70° C. The plating action is self-limiting so that thickness control is not required and overly thick deposits cannot be made.

The 4:1 dilution of "DNS" concentrate recommended by its manufacturer is not preferable, however, as applied to the plating of small parts such as the integrated circuit package 10. The area of a substrate 12 of a typical package 10, for example is about 1.00 inch by 0.33 inch, or 0.33 square inches, and the metallized area thereof which is to be plated is about 10% of this or about 0.03 square inches. The solution at the 4:1 concentration will cost more in losses than the amount required for plating. A large loss occurs when the parts are removed from the plating solution because they emerge wet with the solution, which contains a relatively large amount of palladium. A tank of material suitable for immersing 2,000 or 3,000 lot batches of the

packages 10 would cost several hundred dollars. With repeated usage, the bath deteriorates in palladium and increases in impurity concentration in a linear inverse ratio. Consequently, a point will be reached prior to depletion of all the usable palladium, where the solution can no longer be used. These disadvantages can be obviated by employing a concentration which is dilute enough a predetermined measured to provide an amount of palladium usable for a single lot. If this dilute solution is used for a sufficient time, the required amount of palladium will plate out onto the parts and the residue which will still contain some palladium, can be discarded or reclaimed. Preferably, the plating should be carried out in a slowly turned, sealed, non-metal container.

After the application of the palladium coating 20 the leads 16 and 18 are brazed to the palladium coated molybdenum layer by heating the entire assembly, with the brazing preforms in place, in a belt furnace. Any one of the brazing alloys mentioned above may be used, but a preferred brazing material is a copper-silver alloy which has a eutectic temperature of about 780° C. The maximum temperature in the brazing furnace is about 1,000° C, preferably about 960° C. The total time of brazing is about 45 minutes.

The examples show that the "DNS" plating solution can be diluted as far as 35:1 without adversely effecting the plating. The plating time increases with increased dilution, but the reduction in loss of palladium and the improvement in product quality adequately compensate for this sacrifice. The process can be accelerated by heating if desired.

EXAMPLE 1

In this example, a 4:1 dilution of "DNS Palladium Immersion Solution" was made by diluting 40cc of "DNS" concentrate (50 grams of palladium per liter) with 160cc of deionized water. The diluted solution was heated to 60° C and a quantity of 12 ceramic wafers, having conventionally applied molybdenum coatings thereon, were immersed.

One piece was removed and rinsed in deionized water every 3 minutes for from 3 to 36 minutes. Each piece then had leads brazed thereto in the manner described above, and when brazed all were good. More parts, 2,260 in number, were immersed in the same solution in two batches of 1,130 each for 30 minutes and

in all cases the brazing was good, indicating that the solution was not depleted in the earlier platings and that the minimum time of palladium deposition at this dilution is less than 3 minutes at 60° C.

EXAMPLE 2

In this example, the "DNS" concentrate was diluted 16:1 rather than 4:1 as in the preceeding example. Similar parts were immersed and the plating time was reduced to 10 minutes. The temperature was held at 55° C. All the plated parts were then brazed and the brazes were good.

EXAMPLE 3

A dilution of 35:1 "DNS" produces a palladium ion concentration of only 1 gram per 700cc of solution. Parts were immersed in a solution of the concentration for a period of 60 minutes resulting in a satisfactory plating on each part. Secure joints resulted after brazing.

What is claimed is:

1. A method of bonding metallic bodies to molybdenum-containing bodies comprising the steps of, coating said molybdenum-containing bodies with palladium by immersing said molybdenum-containing bodies in a dilute electroless palladium plating solution, containing a predetermined amount of palladium, for a time sufficient to plate out substantially all of said palladium onto said bodies, and brazing said metallic bodies to the palladium coated molybdenum-containing bodies with a brazed material of silver, copper, or alloys of silver and/or copper.

2. A method as defined in claim 1 wherein said electroless palladium plating solution is a solution of potassium dinitrito-sulphato-palladite and contains palladium ions in a concentration of 1/700 gram per cc.

3. A method as defined in claim 1 wherein each of said molybdenum-containing bodies is a layer comprising molybdenum on and bonded to a body of ceramic material.

4. A method as defined in claim 3 wherein said braze material is a copper-silver alloy having an eutectic temperature of about 780° C, and wherein said brazing operation is carried out at a maximum temperature of about 1,000° C.

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